Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 36 (2010) 1901–1904
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Combustion synthesis of high porosity SiC foam with nanosized grains

J.F. Qiu [a,b], J.T. Li [b,*], K.L. Smirnov [c]

[a] *Graduated School of the Chinese Academy of Sciences, Beijing 100039, PR China*
[b] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China*
[c] *Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka 142432, Russia*

Received 29 June 2009; received in revised form 16 January 2010; accepted 20 March 2010
Available online 27 April 2010

Abstract

High porosity silicon carbide (SiC) foam with nanosized grains was synthesized by a newly developed process involving two steps: (i) preparation of Si/C foam by gel-casting technique and (ii) fabrication of SiC foam by combustion Si/C foam in nitrogen atmosphere. The as-synthesized SiC foam with a high porosity in the range 70–90% exhibited an attractive strength up to 1.6 MPa. SEM analysis showed that the foam struts consisted of tightly bonded SiC particles with a grain size of 80–300 nm.

Keywords: B. Porosity; D. SiC; Combustion synthesis; Physical vapor transportation

1. Introduction

SiC foam has been widely used as diesel particle filters for internal engines, high temperature catalyst carrier and heat insulation materials, due to its unique combination of low thermal-expansion coefficient, good thermal-shock resistance, as well as excellent mechanical and chemical stability at elevated temperature [1–4]. The conventional way of fabrication of SiC foam includes replication technique, gel-casting technique and reaction bonding methods, following by high temperature sintering process [5–7]. However, the great energy consumption and abnormal grain growth were inevitable during the sintering process. Hence, it is significant to develop a new process for producing SiC foams without long time sintering at elevated temperature.

Gel-casting is a new processing route for the fabrication of highly porous ceramics. This method, originally developed by Oak Ridge national laboratory for the fabrication of dense ceramics [8], combines the foaming of aqueous slurry of ceramic powder and organic monomers and the in situ polymerization of the foamed slurry. A successful application of this process is to produce the high strength Al_2O_3 foam with porosity over 85% [9].

Combustion synthesis has been widely used in fabricating many ceramic materials dense and porous due to the short production cycle, high product purity, especially the energy saving nature [10,11]. Direct preparation of high-porous foams by combustion synthesis is also possible by using of gasifying agent or due to impurity degasification in combustion wave [12,13]. However this method is very sensitive to conditions for pore formation and suitable for restricted number of ceramic materials.

The present work is focused on exploring more universal and reproducible fabrication technique of high porosity SiC foam by combining the gel-casting technique with combustion synthesis.

2. Experimental

2.1. Materials and chemicals

The raw starting materials used in this work are silicon (Si) powder (purity, 99%, size, 2–20 μm), activated carbon (C) powder (purity, 99.9%, size, 10–50 nm), and all other reagents used in this work were analytically pure. The Si/C powder mixtures with a mole ratio of 1:1 were used as raw materials for forming the high-porous Si/C foam, and n-Octylamine was used as foaming agent.

For the gel-casting process, acrylamide (AM) was used as monomer, difunctional N,N′-methylenebisacrylamide (MBAM) was coupling agent. The initiator was ammonium persulphate

---

* Corresponding author. Tel.: +86 10 82543693; fax: +86 10 82543693.
E-mail address: ljt0012@vip.sina.com (J.T. Li).

0272-8842/$36.00 © 2010 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2010.03.026

(APS), and the catalyst was N,N,N′,N′-tetramethylethylenediamine (TEMED). Moreover, tetramethylammonium-hydroxide (TMAH) was added into the slurry to control the pH value.

2.2. *Process of synthesis of SiC foam*

The process of synthesis of SiC foam was described in Fig. 1. Previously, an aqueous solution with 6 wt% AM/ MBAM (weight ratio 20:1) was prepared as the premix solution, and then the foaming agent was added into the premix solution by mechanical stirring for 0.5 h, after that the Si/C powder mixtures were added into the above solution till the solid loading in the suspensions reached 50 vol%. The suspension was vigorously stirred for 10 min to generate homogenous foam slurry. Simultaneously, TMAH was added into the slurry to adjust the pH value to 10. The slurry was then poured into a stainless steel mould and kept at 80 °C for monomers polymerization. After monomers polymerized, the green bodies were de-molded and dried at 120 °C under controlled humidity to avoid cracking and non-uniform shrinkage. The dried Si/C foam was loaded directly into a porous graphite crucible, and then the crucible was put into a high pressure vessel for carrying out the combustion synthesis. The high pressure vessel was evacuated to a vacuum degree of 1×10^{-4} MPa followed by backfilling with N_2 to 4 Mpa. The combustion reaction of the Si/C foam was ignited by passing an electric current (10 A) through a tungsten coil placed above the sample. The reaction temperature was recorded by a W-Re3/W-Re25 thermocouple, which was directly inserted into the reactant.

2.3. *Testing method*

The density of the as-synthesized SiC foam was measured by the Archimedes method. The microstructure was investigated by scanning electron microscope (SEM; HITACHIS-4300). Phase composition was conducted by X-ray diffraction analysis (XRD, Rigaku D/max 2550 V, Japan) with Cu Kα radiation, operating at 40 kV and 100 mA. The samples were machined to 3 mm × 4 mm × 40 mm for testing the three-point bending strength (Autograph AG-1, Shimadzu, Japan) with a support distance of 30 mm and a cross-head speed of 0.5 mm/min. The strength was obtained from the average value of five samples measured.

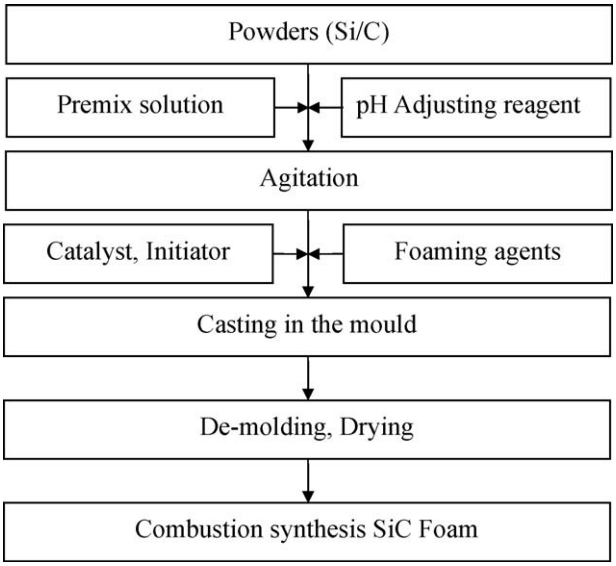

Fig. 1. Flow chart for processing the SiC foam.

3. Results and discussion

The combustion synthesized SiC foams in light green exhibited high porosity and satisfied strength. The typical picture of product with a dimension of 14 cm × 8 cm × 3 cm was shown in Fig. 2. The striations corresponding to the combustion wave propagation were clearly seen on the top surface of the product. The width of each combustion wave zone was about 3 mm. This indicates that combustion reaction in the Si–C–N system probably has taken place by an oscillating mode. The combustion temperature profile of the Si/C foam reactant presented at Fig. 3 also looks typically for oscillating mode. Nevertheless the same temperature profile we may expect in heterogeneous reaction media such as the Si/C foam reactant body [11,14].

X-ray diffraction patterns of the products with different densities are shown in Fig. 4. The major phase in all products

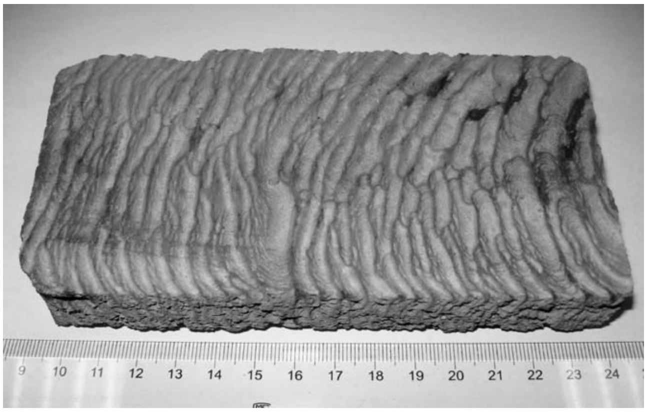

Fig. 2. Photograph of the as-synthesized product.

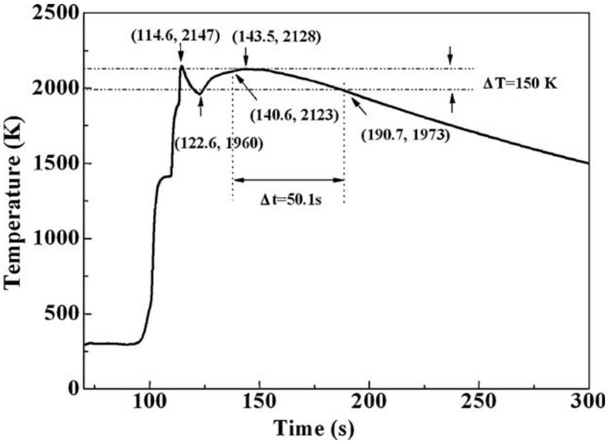

Fig. 3. Combustion temperature profile of the Si/C foam reactant with $\rho = 0.5$ g/cm^3.

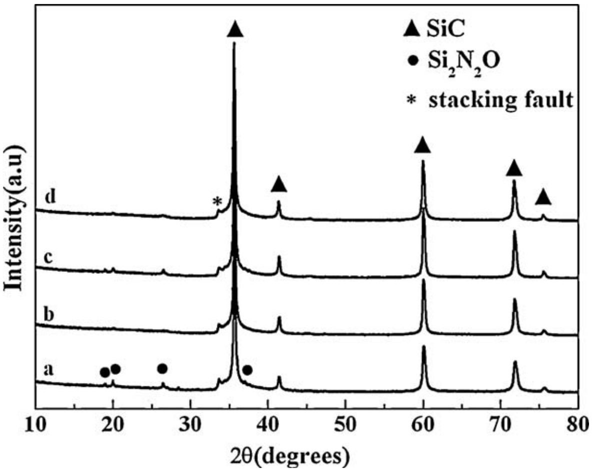

Fig. 4. XRD patterns of the products synthesized from Si/C foam reactants with different densities: (a) $\rho_a = 0.31$ g/cm^3; (b) $\rho_b = 0.50$ g/cm^3; (c) $\rho_c = 0.64$ g/cm^3; (d) $\rho_d = 0.91$ g/cm^3.

was β-SiC, with the trace amount of Si_2N_2O detected. The most detailed description of multistep mechanism of chemical reactions during combustion in the Si–C–N system and its influence on microstructure and phase transformations presented in Ref. [15]. This multistep mechanism implies formation of some amount of Si_3N_4 as intermediate product. In present case, Si_2N_2O may be derived from the reaction between Si_3N_4 and SiO_2. Generally, some SiO_2 (about 0.8 wt%) exists on the surface of Si powder and additional amount of SiO_2 (up to 3 wt%) can arise from the chemical reaction of Si powder with oxygen containing polymer binder. Therefore, the peaks of Si_2N_2O were clearly observed in the XRD patterns.

The maximum combustion temperature and the density of SiC foam were closely related to the density of Si/C foam, as shown in Fig. 5. The porosity of the SiC foam was from 73% to 91%. The floating effect of the as-synthesized SiC foam shown in the inset of Fig. 5 was a good indication of the high porosity reached. With an increase in the density of the Si/C foams from 0.31 g/cm^3 to 0.91 g/cm^3, the corresponding combustion temperature changed from 2123 K to 2195 K.

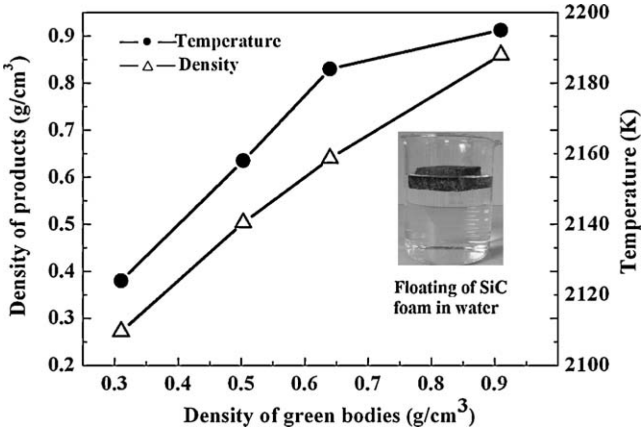

Fig. 5. The dependence of product density and combustion temperature on the density of Si/C foams, and the inset shows the suspension of SiC foam.

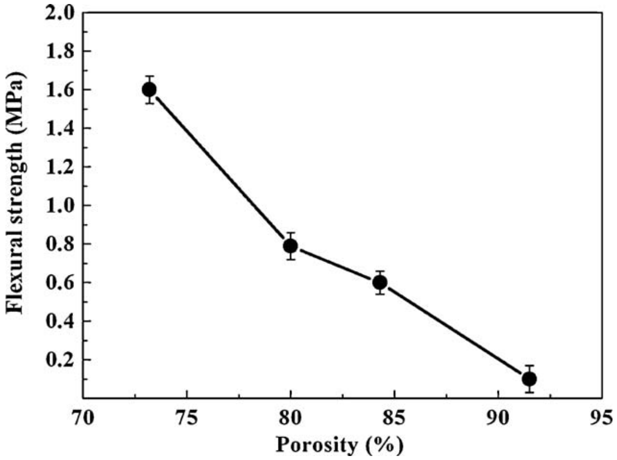

Fig. 6. The strength of SiC foams with different porosities.

As shown in Fig. 6, the strength of the synthetic SiC foam was strongly dependent on its porosity. The maximum flexural strength reached 1.6 Mpa with a porosity of 73.2%. When the porosity increased to 91.5%, the strength decreased to a much lower value of 0.1 MPa. It is also noticed that the strength of SiC foam reached 0.8 MPa at the porosity level of 84.3%, which is high enough for the melt filtering purpose in steel making industry.

SEM images of as-synthesized SiC foam were shown in Fig. 7. It could be observed that the pore size was smaller than

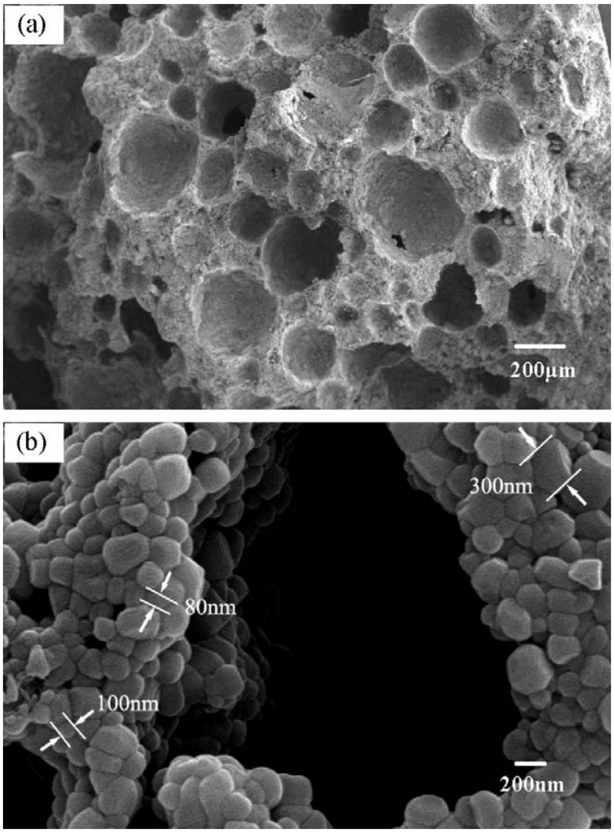

Fig. 7. SEM images of the porous structure in the combustion synthesized SiC foam: (a) the fracture surface and (b) the strut of SiC foam.

300 μm, and the grain size of SiC particles in the foam strut ranges from 80 nm to 300 nm. Most of fine grains were tightly bonded to make up the foam struts, which could be attributed to the high sintering degree in the combustion synthesis process. Such dense struts accorded with the relative high strength of the combustion synthesized SiC foam with porosity of 80%.

According to the solution re-precipitation mechanism, the grain size of SiC powders fabricated by combustion synthesis depends on the starting carbon powder [16]. In present case, the grain size of SiC particle formed in the foam struts was much larger than that of carbon. Meanwhile, Si/C foams were prepared without sintering additives such as Al_2O_3 and/or Y_2O_3, which are typically used for the densification of SiC ceramics. In this way, it is thought that the dense struts with high strength were not produced by the solution re-precipitation mechanism. It has been reported that the sintering of β-SiC ceramics is generally controlled by the evaporation–condensation mechanism with a sintering temperature above 2323 K [17]. However, in our experiments the maximum temperature is only 2123 K in present case, as shown in Fig. 3. The mechanism for the formation of the dense struts in the SiC foam is not very clear at present, which will be investigated later.

4. Conclusions

By combining gel-casting technique with combustion synthesis, SiC foams with high porosities have been prepared. The frame of the foams is composed of fine SiC grains of 80–300 nm, which are tightly bonded and contribute to a high strength. The flexural strength of the SiC foams increases with a decreasing porosity and reaches 1.6 MPa with a porosity of 70%.

Acknowledgment

This work is supported by the National Natural Science Foundation of China under Grant No. 50502035 and 50372074.

References

[1] N. Keller, C. Pham-Huu, S. Roy, M.J. Ledoux, C. Estournes, J. Guille, Influence of the preparation conditions on the synthesis of high surface area sic for use as a heterogeneous catalyst support, J. Mater. Sci. 34 (1999) 3189–3202.

[2] J. She, J. Yang, N. Kondo, T. Ohji, S. Kanzaki, Z. Deng, High-strength porous silicon carbide ceramics by an oxidation-bonding technique, J. Am. Ceram. Soc. 85 (2002) 2852–2854.

[3] M. Benaissa, J. Werckmann, G. Ehret, E. Peschiera, J. Guille, M.J. Ledoux, Structural studies of active carbon used in the growth of silicon carbide catalyst support, J. Mater. Sci. 29 (1994) 4700–4707.

[4] J. Adler, Ceramic diesel particulate filters, Int. J. Appl. Ceram. Technol. 2 (2005) 429–439.

[5] S.Q. Ding, Y.P. Zeng, D.L. Jiang, A colloidal probe microscopy study of cellulose/gypsum interactions, Mater. Charact. 2 (2008) 140–145.

[6] U.T. Studart, E. Gonzenbach, L.J. Tervoort, Gauckler, Processing routes to macroporous ceramics: a review, J. Am. Ceram. Soc. 89 (2006) 1771–1789.

[7] R. Mouazer, I. Thijs, S. Mullens, J. Luyten, SiC foams produced by gel casting: synthesis and characterization, Adv. Eng. Mater. 6 (2004) 340–343.

[8] O.O. Omatete, M.A. Janney, R.A. Strehlow, Gelcasting—a new ceramic forming process, Am. Ceram. Soc. Bull. 70 (10) (1991) 1641–1649.

[9] J. Long, L. Huang, H. Yong, Particle-stabilized foams slurry and manufacturing of porous alumina ceramics, J. Chin. Ceram. Soc. 36 (2008) 220–223.

[10] A.G. Merzhanov, Advanced SHS ceramics: today and tomorrow morning, in: N. Soga, A. Kato (Eds.), Ceramic: Toward the 21st Century, Ceram. Soc. Jap., Tokyo, 1991, pp. 378–403.

[11] A.G. Merzhanov, Wordwide evolution and present status of SHS as a branch of modern R&D, Int. J. Self-Propag. High-Temp. Synth. 6 (2) (1997) 119–163.

[12] V.A. Shcherbakov, A.G. Merzhanov, Self-propagating high-temperature synthesis of cermet foam, Dokl. Ross. Akad. Nauk 354 (1997) 346–349.

[13] S.G. Vadchenko, V.I. Ponomarev, A.E. Sytschev, Self-propagating high-temperature synthesis of porous materials in the Ti–Si–Al–C system, Combust. Explos. Shock Waves 42 (2006) 170–176.

[14] S.G. Vadchenko, A.G. Merzhanov, Heterogeneous model of flame propagation, Dokl. Ross. Akad. Nauk 352 (4) (1997) 487–489.

[15] D. Kata, J. Lis, R. Pampuch, L. Stroberski, Preparation of fine powders in the Si–C–N system using SHS method, Int. J. Self-Propag. High-Temp. Synth. 7 (4) (1998) 475–486.

[16] R. Pampuch, L.S. Ki, J. Lis, Synthesis of sinterable β-SiC powders by a solid combustion method, J. Am. Ceram. Soc. 72 (1989) 1434–1435.

[17] J. Zhang, J.C. Jeong, J.H. Lee, C.W. Won, The effect of carbon sources and activative additive on the formation of SiC powder in combustion reaction, Mater. Res. Bull. 37 (2002) 319–329.